Mechanisms of hydrogen sulfide removal by ground granulated blast furnace slag amended soil

Xie, Mengyao; Leung, Anthony Kwan; Ng, Charles Wang Wai

Published in:
Chemosphere

DOI:
10.1016/j.chemosphere.2017.02.016

Publication date:
2017

Licence:
CC BY-NC-ND

Document Version
Peer reviewed version

Mechanisms of hydrogen sulfide removal by ground granulated blast furnace slag amended soil

Mengyao Xie[1]; Anthony Kwan Leung[2]; Charles Wang Wai Ng[3]

[1]Department of Civil and Environmental Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong (corresponding author). Email: mxieac@connect.ust.hk

[2]Division of Civil Engineering, University of Dundee, DD1 4HN, United Kingdom. Email: a.leung@dundee.ac.uk

[3]Department of Civil and Environmental Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong. Email: cecwwng@ust.hk

Abstract

Ground granulated blast furnace slag (GGBS) amended soil has been found able to remove gaseous hydrogen sulfide (H_2S). However, how H_2S is removed by GGBS amended soil and why GGBS amended soil can be regenerated to remove H_2S are not fully understood. In this study, laboratory column tests together with chemical analysis were conducted to investigate and reveal the mechanisms of H_2S removal process in GGBS amended soil. Sulfur products formed on the surface of soil particle and in pore water were quantified. The test results reveal that the reaction between H_2S and GGBS amended soil was combined process of oxidation and acid-base reaction. The principal mechanism to remove H_2S in GGBS amended soil was through the formation of acid volatile sulfide (AVS), elemental sulfur and thiosulfate. Soil pH value decreased gradually during regeneration and reuse cycles. It is

found that the AVS plays a significant role in H_2S removal during regeneration and reuse cycles. Adding GGBS increased the production of AVS and at the same time suppressed the formation of elemental sulfur. This mechanism is found to be more prominent when the soil water content is higher, leading to increased removal capacity.

Keywords

H_2S, GGBS, sulfur, AVS, regeneration

1. Introduction

Ground granulated blast furnace slag (GGBS) is a by-product of iron and steel industry. Large amounts of GGBS are generated each year (e.g., production capacity of 10 million tons, "K. Wah Construction Material," 2016). GGBS is rich in minerals, finely granulated and highly alkaline. Its most popular use is to replace cement in concrete to improve strength, durability, decrease permeability and retard setting (Oner and Akyuz, 2007). GGBS has also be sometimes used for soil solidification and stabilization (Kogbara and Al-Tabbaa, 2011).

Landfill is a source of odorous gas, mainly in the form of H_2S. The odorous gas would migrate through landfill cover soil and cause serious environmental problems. GGBS has been shown to be an effective soil conditioner to reduce H_2S concentration (Ng et al., 2016). The laboratory study shows that GGBS amended soil could reduce H_2S to a level lower than the olfactory threshold of 0.02 ppm (i.e., the lowest H_2S concentration that human nose could sense), and it can be regenerated multiple times to maintain its removal capacity. The mechanisms involved in H_2S removal and its regeneration/reuse are, however, unclear. Factors that control the capacity of GGBS for H_2S removal are not known.

Linz-Donawitz Steel Slag (LD) and Steel Making Slag (SMS), which have similar composition with GGBS, have been also found effective in removal of H_2S (Kim et al., 2012; Montes-Morán et al., 2012). The existing studies show that elemental sulfur S(0) can be found as a product of the LD-H_2S reaction. Kim et al (2012) estimated sulfur transformation during the removal of aqueous H_2S by SMS and found that the major products were S(0) and manganese sulfide (MnS). Sulfur transformation in unsaturated soil condition (which is often the case for a landfill cover), on the other hand, would be substantially different because soil water content may play a major role. This is because water could influence the physical state of reactant (e.g., gaseous or aqueous), hence the reaction kinetics.

The objective of this paper is to quantify the sulfur transformation and phase transfer upon H_2S removal by GGBS amended unsaturated soil. Sulfur products in soil samples before/after reaction and during each regeneration/reuse cycles were measured. Influences of soil water content on the removal mechanisms are then investigated.

2. Materials and methods

2.1 Material properties

Loess soil (silty clay) was collected from Xi'an, China. GGBS was provided by K. Wah Construction Company, Hong Kong. Loess soil samples were amended with 0% and 30% (by mass) GGBS. pH values of loess and GGBS are 8.36 and 11.67, respectively. pH value of loess amended with 30% GGBS is 11.74. Measurements show that after adding 30% GGBS (mean particle size of GGBS is 9.33 μm), the mean particle size of amended soil shifts from 35.36 μm to 27.87 μm. Metal contents of loess soil and GGBS were obtained using X-ray fluorescence (XRF), and they are summarized in Table 1. Chemico-physical properties of

75 loess, GGBS and their mixtures were measured and are listed in Table 2. Water used in all
76 the tests in this study was ultrapure water. Chemicals were provided by Sigma-Aldrich.
77
78 2.2 Sample preparation and analysis methods
79 Dynamic H_2S removal tests and regeneration tests were carried out. Loess soil was amended
80 with 0% and 30% GGBS, compacted to the same bulk density (1.54 g/cm^3) in a soil column.
81 A concentration of 1000 ppm H_2S was supplied from the bottom of each column at a constant
82 rate of 50 mL/min. The tests would stop when H_2S breakthrough took place. H_2S
83 breakthrough is defined when the H_2S concentration at the column outlet reached the
84 olfactory threshold of 0.02 ppm. H_2S removal capacity is defined as the maximum sulfur
85 (sulfur in H_2S, unit mg) that can be removed by 1 g of soil (bulk mass) before H_2S
86 breakthrough. Regeneration method was air ventilation. Detailed test procedures are reported
87 by (Ng et al., 2016). In order to investigate the effects of soil water content on H_2S removal
88 capacity and removal mechanisms, GGBS amended soils with different gravimetric water
89 contents (i.e., 0%, 10% and 20%) were tested. For the GGBS amended soil with water
90 content of 20%, three regeneration and reuse cycles were applied. The testing program is
91 shown in Table 3.
92
93 After each column test, two soil samples (around 4 g each) were collected from the lower part
94 of the soil column. These two samples were placed into two separate 250 ml pyrex glass
95 bottles, namely A and B. Bottle A was used for the measurements of the concentration of
96 soluble sulfide, sulfate and thiosulfate in soil water, while bottle B was used to measure the
97 concentration of elemental sulfur S(0) and acid volatile sulfide (AVS) on soil particle.
98 Detailed measurement procedures of these chemicals are given in the next section. Both
99 bottles A and B contained 30 ml of ultrapure water and 5 drops of 10 N sodium hydroxide

100 (NaOH), aiming to increase the pH to prevent sulfide ion from forming H_2S. Soil in the bottle
101 A was agitated by magnetic stirrers to facilitate soluble sulfide, sulfate and thiosulfate to
102 dissolve in the water. After agitation, the soil-water mixture was allowed to stand and
103 segregate. A flow chart of chemical measurements can be found in Fig. S1 in the
104 supplementary information (SI). Each condition was tested for two replicates.
105
106 2.2.1 Measurements of soluble sulfide, sulfate and thiosulfate in soil pore water
107 Supernatant from the bottle A was filtered through 0.45 μm filter (Sartorius Stedim), and the
108 filtrate was collected. The filtrate was firstly taken for measuring the concentration of soluble
109 sulfide using the methylene blue method (APHA, 2005). In this method: 1 drop of 10N
110 NaOH was added into 6 ml filtrate sample, and then 0.4 ml amine sulfuric acid and 0.12 ml
111 ferric chloride ($FeCl_3$) solution were added to filtrate sample. The filtrate was mixed and
112 stood for 5 min, and then 1.28 ml diammonium hydrogen phosphate solution was added to
113 the filtrated sample. Subsequently the sample stood for 20 min to let precipitates to settle
114 down, and then the supernatant was collected and measured with methylene blue absorbance
115 at 664 nm using a UV/Vis spectrophotometer (Lambda 25, Perkin Elmer Inc., USA) with a
116 cuvette providing a light path of 10 mm, and a sulfide measuring range of 0 to 1 mg/L.
117
118 5 ml filtrate from the bottle A was also collected and added with a drop of 1 N zinc acetate
119 ($Zn(Ac)_2$) and a drop of 6N NaOH, and it was mixed and allowed to stood for 10 min for the
120 precipitates of ZnS to settle). Then the supernatant was filtered through 0.45 uM filter again,
121 and the filtrate was used for the measurements of soluble sulfate and thiosulfate, by an ion
122 chromatograph (100, Dionex, USA) equipped with a conductivity detector and an IonPac
123 AS9-HC analytical column.
124

125 2.2.2 Measurements of insoluble AVS, elemental sulfur S(0) on soil particle surface
126 Measurements of AVS were performed by acidifying samples (USEPA, 1991). Bottle B was
127 firstly purged with nitrogen gas (N_2). Then 20 ml concentrated hydrogen chloride (HCl) was
128 added to the soil sample, followed by agitating using a magnetic stirrer. Gas generated from
129 the acid-treated soil was stripped into two serial traps filled with 1 N NaOH solution. After
130 the acid treatment, N_2 gas was injected into the acid-treated soil for one hour continuously to
131 remove any remaining H_2S. Details of the testing apparatus are provided in Fig. S2 in the SI.
132 After an hour of N_2 injection, H_2S absorbed in the NaOH solution was quantified using the
133 methylene blue method (APHA, 2005). The amount of sulfide available in AVS was obtained
134 by subtracting the concentration of soluble sulfide obtained from the previous step (section
135 2.2.1) from the concentration of sulfide measured in this procedure.
136
137 S(0) in the soil samples was measured by the revised method suggested by McGuire and
138 Hamers (2000). After the acid treatment and one hour of N_2 purging, the sealed bottle B was
139 added with 20 ml Tetrachloroethylene (C_2Cl_4), and then shaken continuously for four hours
140 in a spinning shaker. Subsequently, C_2Cl_4, which carried extracted S(0), was collected and
141 filtered through 0.2 μm membrane (Sigma-Aldrich). S(0) was measured using a high
142 performance liquid chromatography (HPLC, LC-30AD, Shimadzu, Japan) equipped with a
143 Waters symmetry C18 column (4.6 mm × 150 mm, 5 μm particle size) and a UV detector set
144 at 254 nm. An eluent of 90% acetonitrile + 10% water was used at a flow rate of 1 mL/min.
145
146 It should be noted that any thiosulfate available in the bottle B would turn into sulfur dioxide
147 (SO_2) and S(0) once the soil was treated with concentrated HCl (see Equation [1]). Therefore,
148 in order to analyze S(0) produced during H_2S removal, it is required to subtract S(0)
149 generated from thiosulfate from that measured by HPLC.

$$S_2O_3^{2-} + 2H^+ \longrightarrow SO_2 + S(0) + H_2O \quad [1]$$

Soil samples were collected from each soil column for chemico-physical characterizations. pH measurement was carried out according to the standard ASTM D4972-13 (ASTM, 2001) using a pH meter (Oakton Instruments). Surface elements were identified by an X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD model). Microstructure was investigated using a Scanning electron microscope (SEM, JSM 6300 (JEOL) model).

3. Results and discussions

In this study, the initial sulfur components of soil samples before reacting with H_2S were measured. Therefore, for the results presented herein, all sulfur products refer to the net sulfur product formed by H_2S reaction.

The major sulfur products in the soil during reaction, regeneration and reuse were identified by the XPS spectrum (see Fig. S3 in the SI). According to the XPS spectra data of sulfur species reported by Moulder (1992), the peaks of mineral sulfide, elemental sulfur, thiosulfate and sulfate could be identified in a S(2p) XPS spectra at binding energies of 162.6 eV, 164 eV, 167.8 eV and 168.8 eV (see x-axis in Fig. S3), respectively. Therefore, the major reaction products of H_2S removal by the GGBS amended soil were metal sulfide, elemental sulfur, thiosulfate and sulfate. This suggests that the chemical analysis were able to cover most of the reaction products.

Fig. 1 shows that for LH and L30GH, H_2S input is almost equal to the sum of all the measured sulfur products. This means that the mass balance of sulfur was almost achieved, and most of the sulfur products have been captured in these tests. For LH, almost all H_2S was transferred into elemental sulfur, S(0). This was attributable to the oxidation of H_2S by the minerals available in loess. For L30GH, H_2S was transferred into 68% AVS, 13% S(0), 11% thiosulfate and 6% sulfide. It was found that the form of H_2S present in soil was controlled by the pH value (Haimour et al., 2005; He et al., 2011). S^{2-} is dominant when pH value is higher than 10. On the contrary, when pH is between 8 and 9, HS^- is dominant, whereas no S^{2-} exists in solution for any pH lower than 8. Since the pH value of L is 8.36 (Table 2), HS^- was likely to be the main form of H_2S existed in soil. As shown in Fig. 1, H_2S in the sample LH was mainly oxidized into S(0), and very few sulfide was found. On the other hand, pH value of the soil sample L30G was 11.74 (Table 2), so it is not surprising to find more sulfide in the soil sample. This is similar to LD slag that its strong alkalinity would trigger dissociation of dissolved H_2S into S^{2-} and HS^- (Montes-Morán et al., 2012). The results also show that adding GGBS could suppress the formation of S(0). This seems to indicate that the use of GGBS may be beneficial for improving the H_2S removal capacity in regeneration cycles because precipitation of S(0) on the surface of soil particles could block the reactive sites substantially (Sun et al., 2014). Moreover, adding GGBS to soil increased the production of AVS, probably because of the higher mineral content in GGBS (Table 1) and increased surface activity due to its high alkalinity. The significance of having high AVS production is discussed later.

Fig. 2 (A) shows that sulfide ions decreased during regeneration, and increased during reuse. This was because of the dissolution of H_2S in pore water during the reuse, and the oxidation of sulfide by O_2 during regeneration, according to the following chemical Equation [2].

197

$$2HS^- + 2O_2 + H_2O \longrightarrow S_2O_3^{2-} \quad [2a]$$

$$2HS^- + 4O_2 \longrightarrow 2SO_4^{2-} + 2H^+ \quad [2b]$$

$$2H_2S + O_2 \longrightarrow 1/4S_8 + 2H_2O \quad [2c]$$

198 (Chen and Morris, 1972; Davydov et al., 1998)

199

200 It should be noted that sulfide would be oxidized into different products when supplying
201 different amount of O_2, as indicated in Equation [2]. Although the formation of thiosulfate,
202 sulfate and elemental sulfur through sulfide oxidation also contributed to the overall sulfur
203 transformation, this was only at very small scale because the total sulfide in pore water was
204 low (<0.06 mg/g).

205

206 Fig. 2 (B) shows that AVS decreased during regeneration, and increased during reuse.
207 Previous studies show that some AVS were very sensitive to O_2. For instance, any exposure
208 of AVS to O_2 would change the nature of some potential AVS minerals such as mackinawite
209 and greigite (Rickard and Morse, 2005). Possible mechanisms are given in Equations [3-4]
210 (which use iron mineral as an example; other minerals may apply). It can be seen from Fig. 2
211 (B) that although AVS changed during several regeneration and reuse, its content was within
212 a relatively constant range between 0.3 mg/g – 0.6 mg/g. This may be because part of the
213 AVS acted as a catalyst to remove H_2S (see Equation [3-4]). During regeneration, AVS
214 turned into mineral oxide/hydroxide (e.g., $Fe(OH)_3$), as shown in Equation [3a-d]. While
215 during reuse, mineral oxides/hydroxide reacted with H_2S and AVS was formed again, as
216 shown in Equation [4a-d]. This is the reason why GGBS amended soil could be regenerated
217 to remove H_2S through air ventilation. This is similar to the mechanism when Linz-Donawitz
218 Steel Slag is used to remove H_2S, the reaction during which the transition metal oxides and/or

hydroxides would act as active catalysts to oxidize H_2S to elemental sulfur (Montes-Morán et al., 2012). It should be noted that for Equations [3a-c] and [4a], during both regeneration and reuse, S(0) would be formed, and this may be the reason that caused continuous increase in S(0) from L30GH to R3 (see Fig. 2 (B)).

$$4FeS + 3O_2 + 6H_2O \longrightarrow 4Fe(OH)_3 + 1/2S_8 \quad [3a]$$

$$2Fe_2S_3 + 3O_2 + 6H_2O \longrightarrow 4Fe(OH)_3 + 3/4S_8 \quad [3b]$$

$$2Fe_2S_3 + 3O_2 \longrightarrow 2Fe_2O_3 + 3/4S_8 \quad [3c]$$

$$FeS_2 + 4.25O_2 + 2.5H_2O \longrightarrow Fe(OH)_3 + 2H^+ + 2SO_4^{2-} \quad [3d]$$

$$2Fe(OH)_3 + 3H_2S \longrightarrow 2FeS + 1/8S_8 + 6H_2O \quad [4a]$$

$$2Fe(OH)_3 + 3H_2S \longrightarrow Fe_2S_3 + 6H_2O \quad [4b]$$

$$Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O \quad [4c]$$

$$2Fe_2S_3 \longrightarrow FeS_2 + Fe_3S_4 \quad [4d]$$

(Davydov et al., 1998; Schippers and Jorgensen, 2002).

$$FeS + 1/2O_2 + H_2S \longrightarrow FeS_2 + H_2O \quad [5a]$$

$$2Fe(OH)_3 + 3H_2S + 6O_2 \longrightarrow Fe_2(SO_4)_3 + 6H_2O \quad [5b]$$

$$2Fe(OH)_3 + 6H_2S + 6O_2 \longrightarrow Fe_2(S_2O_3)_3 + 9H_2O \quad [5c]$$

(Cantrell et al., 2003)

In Fig. 2 (A), the measured increase in sulfate ion during regeneration is likely to be attributable to the oxidation of pyrite (Equation [3d]), as well as the oxidation of sulfide (Equation [2b]). Biological oxidation of other reduced sulfur products might be another reason that caused the increase in sulfate through R2 to R3. Sulfur oxidizing bacteria (SOB)

would use the energy of reduced sulfur compounds (e.g., H_2S, thiosulfates, sulfites, and elemental sulfur), and then convert the reduced sulfur compounds to sulfate. The optimum pH values for SOB growth are typically between 1 and 9 (Pokorna and Zabranska, 2015). As can be seen in Fig. 3, during regeneration and reuse cycles, the pH value showed a decreasing trend from about 12 to 9. Thus, it is likely that SOB has been activated and produced sulfate through biological oxidation. The observed pH drop in Fig. 3 was attributable to the dissolution of H_2S during reuse, and oxidation of sulfide ion and pyrite during regeneration. As indicated in Equation [2b] and [3d], both processes would produce hydrogen ion, hence results in decrease of pH value. At R3, the pH value was still around 9, indicating that HS^- and S^{2-} both existed and they were stable in the pore water.

On the other hand, the observed increase in thiosulfate during both regeneration (except for R2) and reuse (see Fig. 2 (B)) is likely to be the consequence of the oxidation of sulfide (Equation [2a]) and the aerobic reaction between mineral hydroxide and H_2S during reuse (Equation [5c]). Since oxygen might dissolve in pore water during regeneration, aerobic reactions might have taken place between H_2S and the soil, hence leading to the production of sulfate and thiosulfate during reuse. When comparing the reaction products from initial H_2S removal (i.e., L30GH) and the removal after regeneration (i.e., R1H and R2H), it demonstrates that there was a change in removal mechanism. For the initial H_2S removal, the main reaction product was AVS (Fig. 1), indicating that most H_2S was bonded with the minerals in the soil. For H_2S removal in the subsequent regenerated cycles, S(0) was accumulated while AVS remained at 0.3 mg/g – 0.6 mg/g (Fig. 2 (B)). This indicates that during regeneration/reuse cycles, the major removal mechanism of H_2S was through the oxidization to S(0).

SEM images depicted in Fig. 4 show that for R3 (where most sulfur products were found compared to others), needle-like elemental sulfur crystal could be identified and it spreads around the surface of soil particles. Small amount of octahedral pyrite can also be seen. This further confirms the proposed removal mechanisms discussed in Equation [3], [4] and [5]. Moreover, because the metal hydroxide/oxide generated from oxidation of AVS acted as a catalyst during the removal of H_2S, the H_2S removal capacity would not change much during each reuse cycle due to relatively constant range of AVS (Fig. 2 (B)). However, precipitation of elemental sulfur on particle surface would gradually reduce the availability of reactive sites and hinder further regeneration and reuse (Sun et al., 2014). Therefore, the H_2S removal capacity was gradually reduced at the subsequent regeneration/reuse cycles (Ng et al., 2016).

Fig. 5 shows the effects of different soil water contents on the removal capacity and removal mechanisms. The removal capacity increased with an increase in soil water content from 0% to 20%. This appears to agree with the findings reported by Montes-Morán et al (2012) who showed that the relative humidity of the slags particles changed dramatically with the H_2S removal capacity. The water solubility of H_2S is relatively high: 7100 mg/L at 0 °C, and 3925 mg/L at 20 °C (Bergersen and Haarstad, 2008). Therefore, higher soil water content would result in more H_2S dissolving in the pore water, and hence more H_2S could be removed from its gas phase. Also, for a given soil dry density, increasing soil water content would decrease the pore air ratio. This would hence (i) reduce the effective diffusion coefficient, and therefore more effectively limit H_2S migration and (ii) extend the retention time of H_2S in the soil, resulting in a higher H_2S removal capacity (Xu et al., 2014). Moreover, it can be seen in Fig. 5 that higher soil water content facilitated AVS formation and suppressed the formation of elemental sulfur. The AVS content increased from 0.166 to 0.527 mg/g (in percentage: from 36% to 68%), while the elemental sulfur decreased from 0.259 to 0.0988 mg/g (from

56% to 13%). Since AVS plays an important role in H_2S removal during regeneration/reuse cycles (see Fig. 2 (B)), increasing AVS content by increasing soil water content is likely to be able to improve H_2S removal capacity during regeneration. Because the accumulation of elemental sulfur would block the availability of reactive sites on the surface of soil particle, reducing elemental sulfur production by increasing soil water content may also improve H_2S removal capacity in regeneration cycles. The test results imply that GGBS amended soil would be suitable to be used as in a landfill cover located in humid regions, because the increase in soil water content due to rainfall could improve the H_2S removal capacity for not only the initial removal but also probably the removal in the subsequent regeneration/reuse cycles.

In Figs 5 and 6, it can be seen that for the first two regeneration cycles of the sample with 20% of soil water content (i.e., from L30GH to R2 in Fig. 6), the removal capacities were almost equal to the sum of the measured sulfur products. For the third regeneration cycle of the samples (i.e., R2H and R3 in Fig. 6) and samples with lower water content (i.e., 0% and 10% in Fig. 5), however, the sum of the measured sulfur products were higher than the removal capacities. This inconsistency may be associated with the reduction of reaction kinetics between H_2S and those samples. It was demonstrated by Xu et al (2014) that in a diffusion-advection-reaction system, any change of reaction kinetics could affect the distribution of H_2S in a soil bed. Hence, a non-uniform distribution of sulfur products along the soil column would be resulted, where the lower part would contain higher sulfur products, whereas the higher part contains less. Since the soil samples tested in the present study were taken at the lower part of the soil columns, their sulfur products content would be higher than the average sulfur content calculated from H_2S input.

4. Conclusions

This study presents a set of comprehensive laboratory testing that provides insights into the pathways and mechanisms of how H_2S would be removed by GGBS amended soil. The test results show that gaseous H_2S could be removed by the GGBS in soil through oxidation and acid-base combined reactions. Using GGBS to react with H_2S caused an increase production of acid volatile sulfide (AVS) and suppressed the formation of elemental sulfur. AVS has shown to play an important role in H_2S removal during regeneration and reuse cycles. Soil pH value gradually decreased during regeneration and reuse cycles. Precipitation of elemental sulfur on particle surface was unfavorable for H_2S removal. Increasing water content of GGBS amended soil up to a 20% (by weight) is favorable for H_2S removal because this promoted H_2S dissolution, simultaneously facilitating the formation of AVS and suppressing the formation of elemental sulfur.

Acknowledgements

The authors would like to acknowledge the research grant grant (HKUST6/CRF/12R) provided by the Research Grants Council (RGC) of the Hong Kong Special Administrative Region. The second author would also like to acknowledge the research travel support from the Northern Research Partnership (NRP).

References

APHA, 2005. Standard methods for the examination of water and wastewater. Washington, DC, USA.

ASTM, I., 2001. Standart Test Method for pH of Soils. ASTM D4972 - 01. ASTM Stand. Test 1, 1–5. doi:10.1520/D4972-01R07.2

Bergersen, O., Haarstad, K., 2008. Metal oxides remove hydrogen sulfide from landfill gas

produced from waste mixed with plaster board under wet conditions. J. Air Waste Manage. Assoc. 58, 1014–1021. doi:10.3155/1047-3289.58.8.1014

Cantrell, K.J., Yabusaki, S.B., Engelhard, M.H., Mitroshkov, A. V., Thornton, E.C., 2003. Oxidation of H_2S by iron oxides in unsaturated conditions. Environ. Sci. Technol. 37, 2192–2199. doi:10.1021/es020994o

Chen, K., Morris, J., 1972. Kinetics of Oxidation of Aqueous Sulfide by O_2. Environ. Sci. Technol. 6, 529–537. doi:10.1021/es60065a008

Davydov, A., Chuang, K.K.T., Sanger, A.A.R., 1998. Mechanism of H_2S oxidation by ferric oxide and hydroxide surfaces. J. Phys. Chem. 102, 4745–4752.

Haimour, N., El-Bishtawi, R., Ail-Wahbi, A., 2005. Equilibrium adsorption of hydrogen sulfide onto CuO and ZnO. Desalination 181, 145–152. doi:10.1016/j.desal.2005.02.017

He, R., Xia, F.F., Wang, J., Pan, C.L., Fang, C.R., 2011. Characterization of adsorption removal of hydrogen sulfide by waste biocover soil, an alternative landfill cover. J. Hazard. Mater. 186, 773–778. doi:10.1016/j.jhazmat.2010.11.062

K. Wah Construction Material, 2016. URL http://www.kwcml.com/en/slag.php

Kim, K., Asaoka, S., Yamamoto, T., Hayakawa, S., Takeda, K., Katayama, M., Onoue, T., 2012. Mechanisms of hydrogen sulfide removal with steel making slag. Environ. Sci. Technol. 46, 10169–10174. doi:10.1021/es301575u

Kogbara, R.B., Al-Tabbaa, A., 2011. Mechanical and leaching behaviour of slag-cement and lime-activated slag stabilised/solidified contaminated soil. Sci. Total Environ. 409, 2325–2335. doi:10.1016/j.scitotenv.2011.02.037

McGuire, M., Hamers, R.J., 2000. Extraction and quantitative analysis of elemental sulfur from sulfide mineral surfaces by high performance liquid chrmatography 34, 4651–4655.

Montes-Morán, M.A., Concheso, A., Canals-Batlle, C., Aguirre, N. V, Ania, C.O., Martín,

M.J., Masaguer, V., 2012. Linz-Donawitz Steel Slag for the Removal of Hydrogen Sulfide at Room Temperature. Environ. Sci. Technol. 46, 8992–8997. doi:10.1021/es301257c

Moulder, J.F., 1992. Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, illustrate. ed. Physical Electronics Division, Perkin-Elmer Corporation.

Ng, C.W.W., Xie, M., Leung, A.K., 2016. Removal of hydrogen sulfide using soil amended with ground granulated blast furnace. J. Environ. Eng. ASCE (In press).

Oner, A., Akyuz, S., 2007. An experimental study on optimum usage of GGBS for the compressive strength of concrete. Cem. Concr. Compos. 29, 505–514. doi:10.1016/j.cemconcomp.2007.01.001

Pokorna, D., Zabranska, J., 2015. Sulfur-oxidizing bacteria in environmental technology. Biotechnol. Adv. 33, 1246–1259. doi:10.1016/j.biotechadv.2015.02.007

Rickard, D., Morse, J.W., 2005. Acid volatile sulfide (AVS), Marine Chemistry. doi:10.1016/j.marchem.2005.08.004

Schippers, A., Jorgensen, B.B., 2002. Biogeochemistry of pyrite and iron sulfide oxidation in marine sediments. Geochim. Cosmochim. Acta 66, 85–92. doi:10.1016/S0016-7037(01)00745-1

Sun, J., Zhou, J., Shang, C., Kikkert, G.A., 2014. Removal of aqueous hydrogen sulfide by granular ferric hydroxide-Kinetics, capacity and reuse. Chemosphere 117, 324–329. doi:10.1016/j.chemosphere.2014.07.086

USEPA, 1991. Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment. United States.

Xu, Q., Powell, J., Jain, P., Townsend, T., 2014. Modeling of H_2S migration through landfill cover materials. J. Hazard. Mater. 264, 254–260. doi:10.1016/j.jhazmat.2013.11.005

382
383 **Table 1. Metal content (weight percentage of dry matter) obtained from XRF analyses**

Type	CaO	SiO_2	Al_2O_3	MgO	TiO_2	K_2O	MnO	Fe_2O_3
Loess	22.8	61.1	7.6	10.5	0.8	1.3	0.0	3.6
GGBS	37.9	34.2	13.8	8.1	1.0	0.6	0.5	0.3

384
385
386
387 **Table 2. Properties of loess and amended loess tested in this study**

Soil condition	ID	G_s (kg/m^3)[a]	pH value[b]	Mean particle size (μm)[b]	S_s (m^2/g)
Loess	L	2690	8.36	35.36	22.58
Loess+30% GGBS	L30G	2760	11.74	27.87	15.95
GGBS	-	2924	11.67	9.33	1.28

388 [a]G_s is specific gravity
389 [b] Mean value of three repeated tests
390

391

392 **Table 3. Testing program**

393
394

Soil condition	Water content	Regeneration cycle	Sample ID*	
			Before H_2S	After H_2S
Loess	15%	-	L	LH
Loess + 30%GGBS	20%	-	L30G	L30GH
Loess + 30%GGBS	20%	1	R1	R1H
		2	R2	R2H
		3	R3	-
Loess + 30%GGBS	0%	-		
	10%			
	20%			

* RX is the soil sample after the X^{th} cycle of regeneration, RXH is the soil sample RX after reacting with H_2S. For example, R1 is the soil sample L30GH after the 1^{st} cycle of regeneration. R1H is the soil sample R1 after reacting with H_2S. R2 is the soil sample R1H after the 2^{nd} cycle of regeneration.

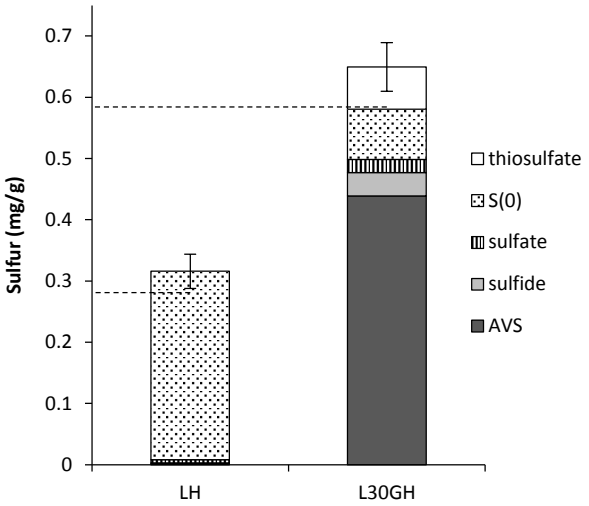


Fig. 1. Sulfur products in soil after reaction with H_2S. Dotted lines represent H_2S input calculated from column tests, error bars represent mean absolute deviation. Sulfur content in y-axis is expressed as mg of sulfur per 1 g of bulk soil.

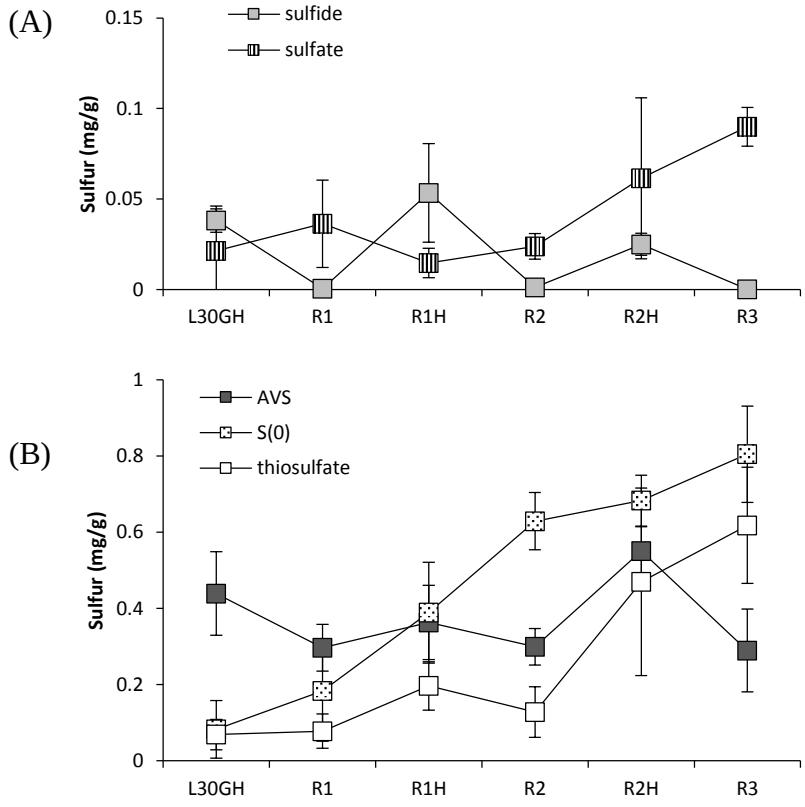
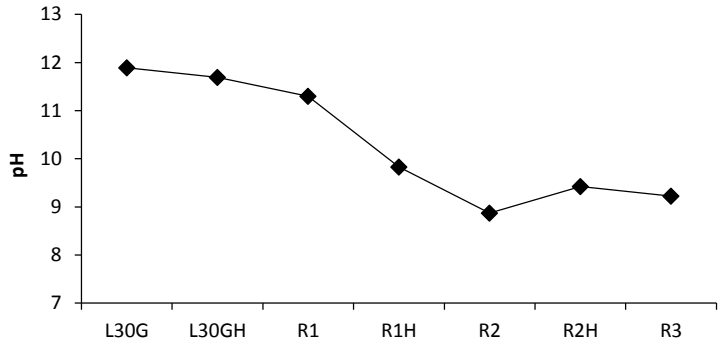


Fig. 2. Sulfur transformation in regeneration/reuse of L30G. Error bars represent mean absolute deviation. Sulfur content in y-axis is expressed as mg of sulfur per 1 g of bulk soil.

409
410
411



412
413

Fig. 3. pH value of L30G during regeneration and reuse

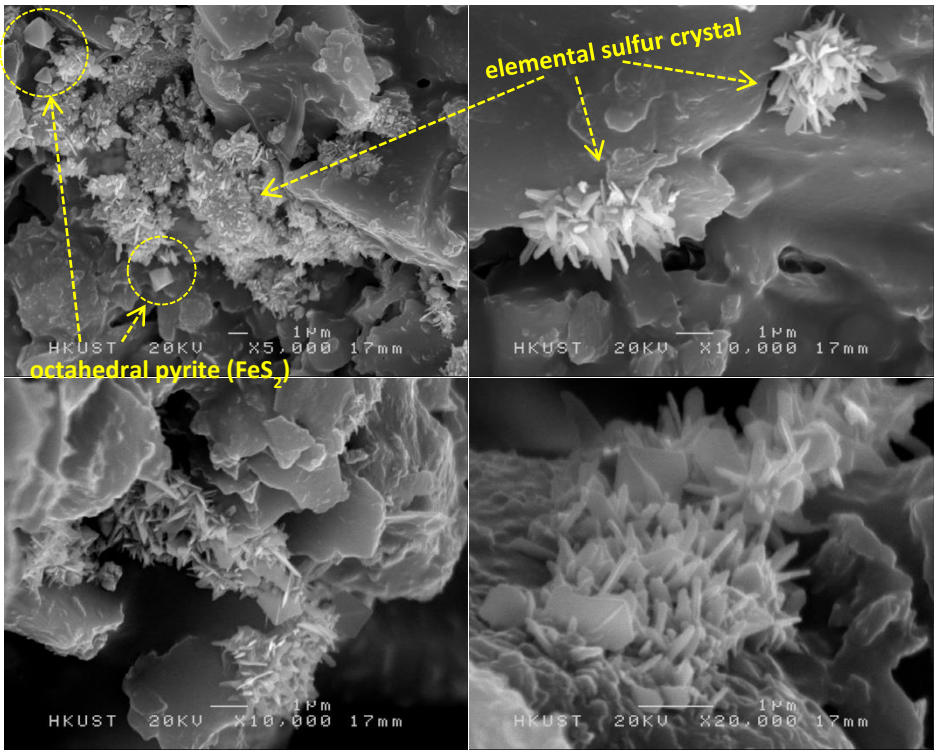


Fig. 4. SEM image of R3 to show the formation of elemental sulfur crystal and octahedral pyrite after reaction

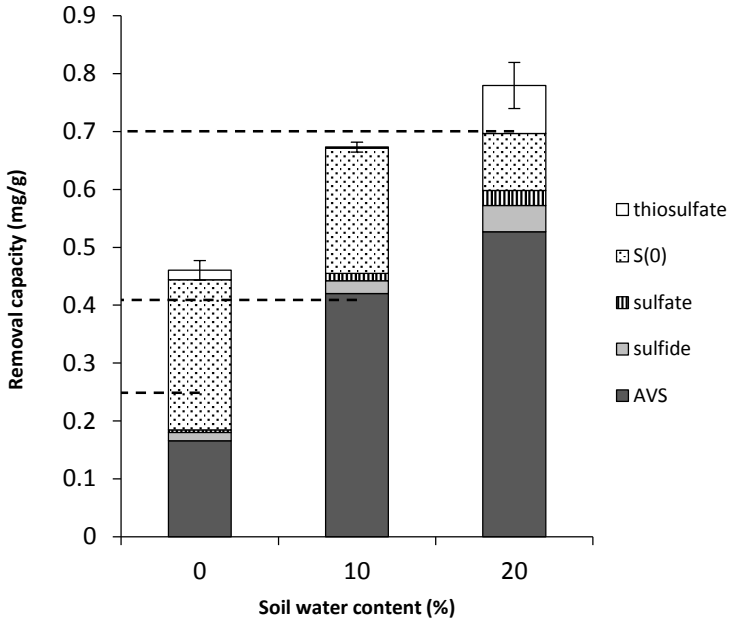


Fig. 5. Influence of water content on sulfur product. Dotted lines represent H_2S input calculated from column tests. Error bars represent mean absolute deviation. Sulfur content in y-axis is expressed as mg of sulfur per 1 g of dry soil.

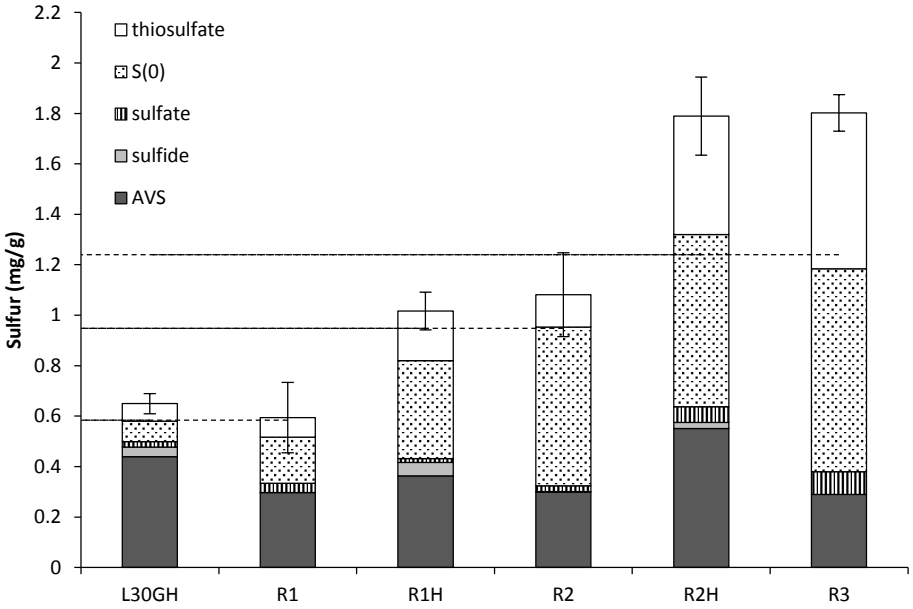


Fig. 6. Sulfur products in L30G regeneration and reuse. Dotted lines represent H_2S input calculated from column tests. Error bars represent mean absolute deviation. Sulfur content in y-axis is expressed as mg of sulfur per 1 g of bulk soil.

Supporting information

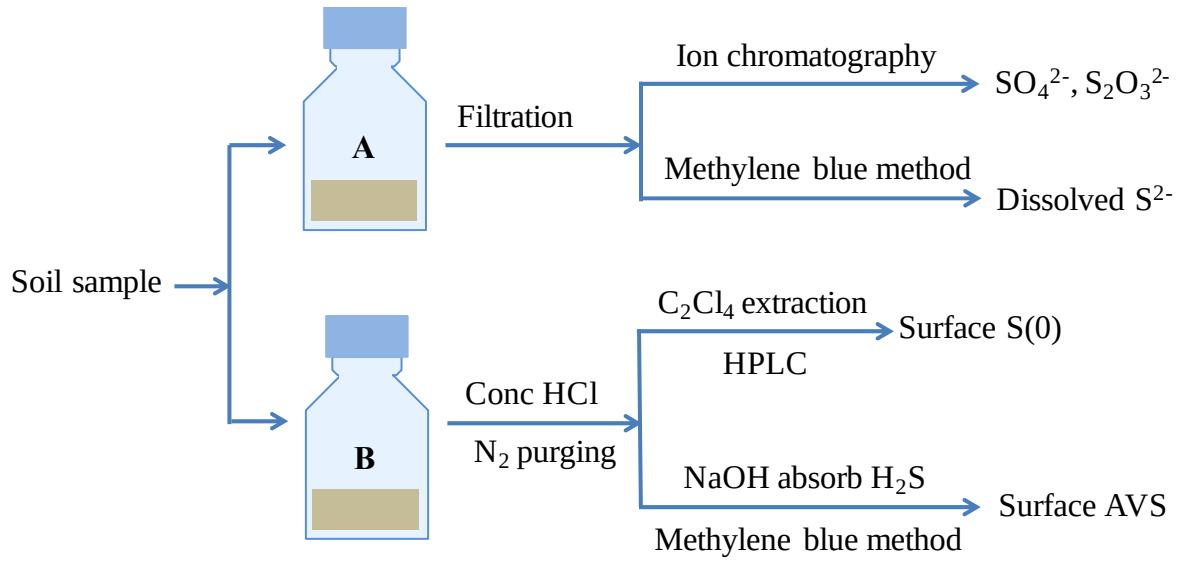


Fig. S1. Flow chart of chemical measurements

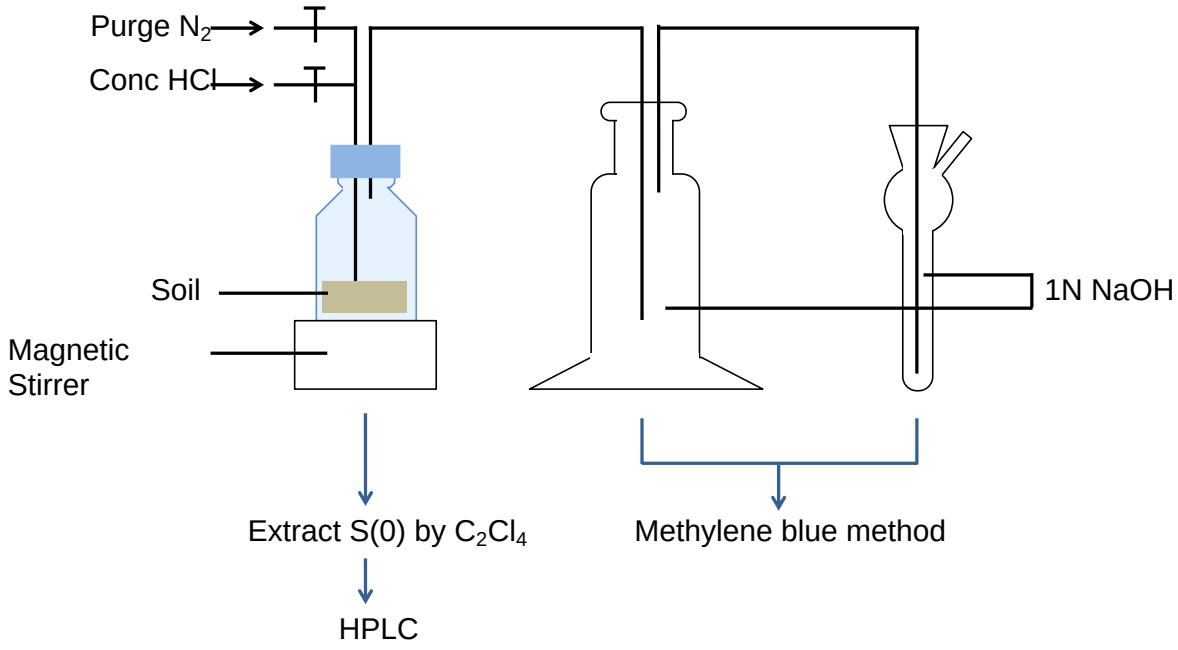


Fig. S2. Test setup for measurement of S(0)

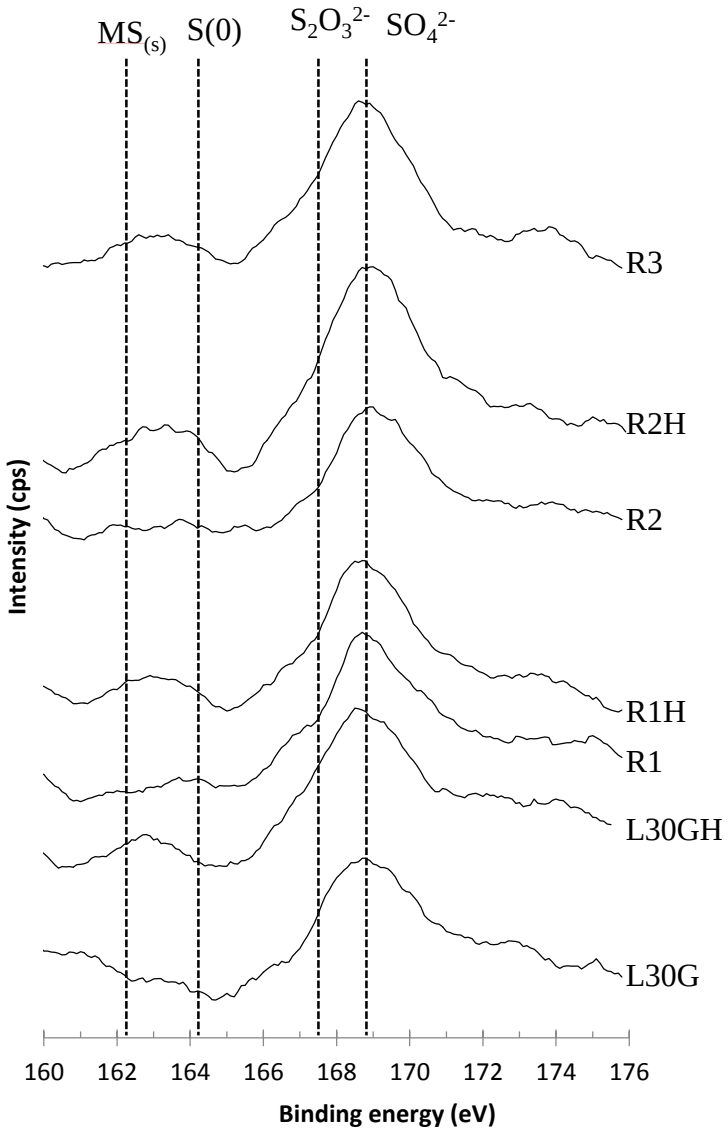


Fig. S3. XPS results of sulfur products in soil samples